

JACOBSON

Analytical control of water softening

Chemistry

M. S.

1910

UNIVERSITY OF ILLINOIS  
LIBRARY

Class

1910

Book

J157

Volume

Mr10-20M







ANALYTICAL CONTROL OF WATER SOFTENING

BY

ANDREW JACOBSON

B. S. St. Olaf College, 1906

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1910

1910  
J157

1410  
5157

1 - 23 Feb 1910

UNIVERSITY OF ILLINOIS  
THE GRADUATE SCHOOL

June 4, 1910 190

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

ANDREW JACOBSON, B. S., ST. OLAF COLLEGE, 1906.

ENTITLED ANALYTICAL CONTROL OF WATER SOFTENING

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

*Edward Bartow*

in Charge of Major Work

*W. A. Noyes*

Head of Department

Recommendation concurred in:

\_\_\_\_\_

\_\_\_\_\_

}

Committee

on

Final Examination

168115

8





UNIVERSITY OF ILLINOIS

June 4, 1910 190

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Andrew Jacobson, B. S. St. Olaf College, 1906.

ENTITLED Analytical Control of Water Softening

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Science

Edward Bartow

Instructor in Charge

APPROVED:

W. A. Noyes

HEAD OF DEPARTMENT OF

Chemistry



Digitized by the Internet Archive  
in 2013

<http://archive.org/details/analyticalcontro00jaco>

## INTRODUCTION.

Water is used in practically all modern human industries in quantities so vast and applications so various and its quality is so different that the question of water supply is one of the most important considerations in the establishment of an industry.

The importance of the quality of a water varies with the purposes for which it is to be used. A highly mineralized water is not suitable for use in steam making and in the household if for no other reason than that it is uneconomical. Iron bearing waters cannot be used in some industries and arts because of the tendency it has to stain. All industries using large quantities of water must have a relatively pure water, or at least a water suited to its specific purpose.

All natural waters contain salts in solution. The kind and quantity depending on the nature of the soils with which it comes in contact.

The substances commonly found are the nitrates, chlorides, sulphates and carbonates of the alkalies, alkaline earths, iron and aluminium, besides silica and organic matter in solution and suspension. Even rain water is not entirely pure, containing dissolved gases such as carbondioxide, oxygen, ammonia and during thunder showers nitric acid.\* Most of these substances interfere

---

\*E. G. Bashore. M. & C. E. Vol. VIII, No. 1.

---

with industrial processes in the quantities in which they are found in natural waters.





The keen competition existing between manufacturers and users of water for steam and other purposes has resulted in a search for means of reducing the cost of production. Such a reduction can be easily accomplished by the addition of certain reagents to the raw water for the purpose of purifying or softening it.

The knowledge that a water is of good quality or the knowledge of the method of purifying and controlling the purification of a water of poor quality is essential.

In this thesis will be given a brief account of the constituents found in a water, a historical statement concerning the development of methods of purifying water for various uses, the reasons why methods of purification are necessary, statements concerning the methods of analysis and control used by others and finally a description of experiments carried out by the writer.



## HISTORICAL.

In 1841 Clark patented his method for the softening of water with lime. Later Porter\* modified the process by filtering

---

\* J. S. C. I. Vol. 3, 1884.

---

the water after precipitation with lime, thus making the softening process continuous.

In the Clark-Porter process the amount of lime to be added was calculated from a determination of alkalinity and total hardness. This method removed only the temporary hardness.

Wm. Macnall and G. H. Beckett\* discovered in 1886 that

---

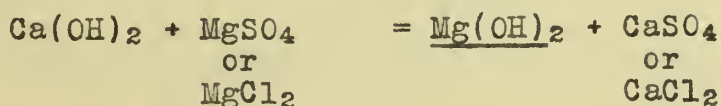
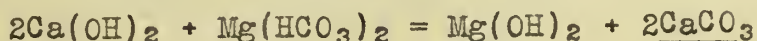
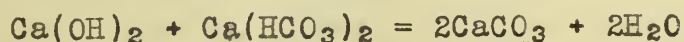
\* J. S. C. I. 5-267.

---

caustic soda or lime and soda were absolutely necessary for the removal of all the magnesium. At present lime and soda ash are invariably used for outside treatment.

Sodium carbonate or hydrate together with various organic substances are sometimes used for treatment in the boiler.

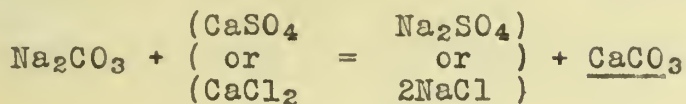
Calcium in the form of hydrate stands first in importance of the substances used in treatment because of its low cost, effectiveness and ease of application. The reactions are:





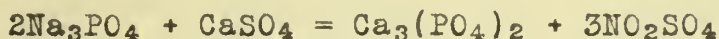


As is apparent from the reactions,  $\text{CaSO}_4$  or  $\text{CaCl}_2$  are not precipitated on the addition of lime. Sodium carbonate must be added to decompose these salts. The reactions are:



Sodium hydrate may be used in place of lime. Its chief objection is its high cost.

Tri sodium phosphate may also be used. It reacts with  $\text{CaSO}_4$  as follows:



This substance is expensive and unless some methods are discovered whereby the phosphate may be regained it will hardly come into general use. Sodium flouride may be used. Its reaction is identical with that of soda, but it is many times more expensive.

Barium hydrate is an ideal reagent because its carbonate or sulphate are insoluble and it leaves no salt in solution in the softened water. It is, however, unimportant as a water softener because of its high cost. There is also an element of danger in its use since it is poisonous.

Various other reagents have been proposed, such as Barium Aluminate, Sodium Aluminate, Chromate and Oxalate of Sodium. Their chief objection is the cost.

Oils, fats, starch, glucose and other organic compounds are sometimes fed to the boiler. Their action, if any, is purely mechanical in preventing the sulphate and carbonate from forming a hard scale.



## REASONS FOR TREATMENT.

Water is treated for the purpose of removing as completely as possible the suspended and dissolved solids. The suspended matter may consist of clay,  $\text{SiO}_2$  and undecomposed organic matter. The dissolved matter that we aim to remove by treatment is Ca, Mg. Iron and Al, commonly found in combination with Cl,  $\text{NO}_3$ ,  $\text{SO}_4$  Bicarbonates and sometimes  $\text{PO}_4$ .

The greatest importance must be attached to waters used for making steam because of its action of boilers. "Steammaking may be regarded as an industry in which the raw material is water and the finished product is steam." Of great interest, therefore, is the quality of water used in the boiler because upon it depends the profitable production of steam.

The life of a boiler using non-corrosive non-scaling water is figured at 30 to 35 years, while a corrosive water may make a boiler useless in 5 years.

The Harrison Safety Boiler Works Company in their "Purification of Boiler Feed Water" outlines the extra cost of steam production resulting from the use of untreated water as follows:

1. The extra coal that must be consumed in order to force the heat through the scale that forms in boilers.
2. The extra cost of putting in additional boilers to supply the steam that the present boilers would furnish if they were kept clean so that they would give full capacity.
3. The extra cost of boiler cleanings, replacements





and repairs.

4. The extra cost of firing up boilers put out of use, service for repairing, cleaning, etc.

5. The cost in annual depreciation charge on boilers the life of which is greatly shortened by corrosion, pitting, forcing, cleaning, expansion and concentrated strains, etc.

The action of water on boilers may be summarized as follows:

1. Incrustation,
2. Corrosion
3. Foaming and Priming

Incrustation is due to one or more of the following causes\*.

---

\*Boiler Waters. Christie, p. 46.

---

1. Deposition of calcium and magnesium carbonates, due to the boiling off of carbon dioxide gas from the water in which they were dissolved.

2. Deposition of sulphate of lime, due to high temperature in the boiler.

3. Deposition of magnesium compound due to their decomposition in the boiler.

4. Deposition of sand, clay and other matter that was suspended in the water.

5. Deposition of alkalie salts due to concentration.

The carbonates of calcium and magnesium are normally



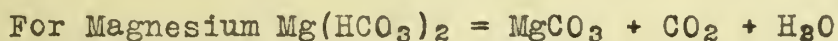
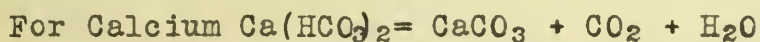
present in water in the form of bicarbonates  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ . The former is soluble to the extent of 1100 parts per million and the latter 27500 parts per million\*.

---

\*Purification of Water for Boiler Feeding. p. 16.

---

At the temperature of boiling water carbon dioxide is liberated and the normal carbonates which are practically insoluble are formed according to the following reaction:



The rather soluble  $\text{MgCO}_3$  is supposed to become insoluble after prolonged boiling\*.

---

\*Purification of Water for Boiler Feeding, p. 16.

---

The carbonates of calcium and magnesium do not form a hard scale but deposits as a soft scale or sludge unless sulphate of calcium is present when it also is cemented into a scale.

Calcium sulphate is the most troublesome of the calcium salts. It forms a hard tenacious scale difficult to remove. Mixed with carbonates, silica and mud it renders the resultant scale hard.

Calcium sulphate is a poor conductor of heat and therefore reduces the evaporative efficiency of the boiler considerably. Rankin in his "Mechanics" gives the relative resistance to the passage of heat of calcium sulphate as 48, wrought iron being taken as 1.





It is a peculiar property of calcium sulphate that it becomes less soluble as the temperature rises. The solubility of calcium sulphate in grains per gallon is as follows:\*

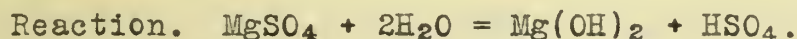
---

\*Engineering. Dec. 25, 1903.

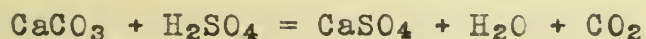
---

Temperature	Steam pressure	Solubility
F.	lbs.	
68	---	140.6
356	131	15.7

Magnesium sulphate is very soluble in water and does not as such form scale. At a temperature of about 350°F it begins to decompose forming insoluble magnesium hydrate and sulphuric acid.



If calcium carbonate is present the acid reacts as follows:



The two together form an extremely hard scale.

Magnesium nitrate and magnesium chloride acts similarly to magnesium sulphate. They are, however, less frequently found in water.

Natural waters always have small amounts of silica in solution (probably in a colloidal state) and frequently sand and clay in suspension, these when present together with the other scale forming ingredients, form a very hard and refractory scale.

The alkalie salts, being very soluble, do not form scale unless a very great concentration has been reached.



E. G. Bashore\* says on this point that an excess beyond

---

\*M. & C. E. Vol. VIII. No. 1. p. 21.

---

300 grains per gallon will cause these salts to be incorporated in the scale.

As already noted scale forming waters add to the cost of production of steam by decreasing the **evaporative** power. According to experiments carried on at the University of Illinois\* the

---

\*Railroad Gazette, June 14, 1901.

---

decrease in the evaporative power of a locomotive boiler was found to be 9.55% for scale  $3/64$  inch in thickness.

The increased heat that must be applied in order to bring the water up to the desired temperature caused the boiler plates to be overheated and weakened and thus may cause serious explosion.

Although no hard and fast rule can be laid down as to the amount of scale forming impurities allowable in a good boiler feed water the following classification is due to Christie\*:

---

\*Boiler Waters. p. 37.

---

Less than 8 grains of incrusting solids per gallon	Good
8 to 15 grains per gallon	Fair
15 to 20     "     "     "	Poor
20 to 30     "     "     "	Bad
30 to 40     "     "     "	Very bad





## CORROSION.

Corrosion is one of the most serious difficulties met with in boiler practice. It may be due to one or more of the following causes:

1. Dissolved gases such as oxygen.
2. Fatty acids due to the decomposition of animal and vegetable matter.
3. Hydrochloric, Nitric and Sulphuric acids due to the decomposition of their salts at high temperatures.
4. Galvanic action.

It is generally known that water containing oxygen is more corrosive than water that is free from oxygen. Although this subject is not thoroughly understood it is thought that oxygen acts as a depolarizer and in this way facilitates the passage of galvanic currents.

In "Purification of Water For Boiler Feeding" we read:

"It has been repeatedly noted that water which has been thoroughly saturated with air and consequently with oxygen, is especially corrosive when used as feed water. In fact, some of the most injurious cases of corrosion can be found where distilled water is used, distilled water having been allowed to become saturated with oxygen from the air".

Organic matter taken into the boiler in the form of oil or grease decomposes under boiler conditions forming fatty acids which attack and corrode the iron. The partly decomposed and heavier parts of the grease attach themselves to small particles in water finally depositing on the tubes and sheets. This



material, being a poor conductor of heat, retards the transmission of heat to the water, causing the metal to be overheated and softened. The result is bulging or bagging of the metal. It has been figured\* that a film of grease 0.01 inch thick, a layer of scale 0.1 inch thick and a steel boiler-plate 10 inches thick offer

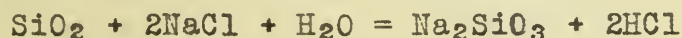
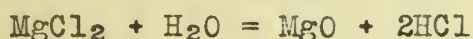
---

\*Christie. Boiler Waters. p. 136

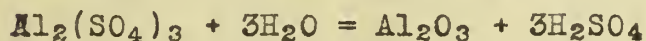
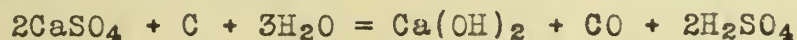
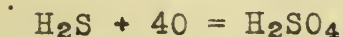
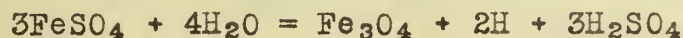
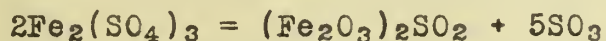
---

the same resistance to the passage of heat. In other words, grease offers about 1000 times and scale 100 times the resistance of steel.

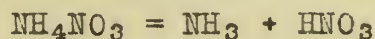
Under conditions of the boiler salts of the mineral acids are supposed to decompose, forming free acids. Hydrochloric acid may be formed as follows:



Sulphuric acid may be formed by the following reactions:



Nitric acid may be formed from the decomposition of nitrates as:



Galvanic action is thought to be due to the settling up



of electric currents between different parts of the boiler. This phenomenon is intensified by the presence of oxygen in the water which acts as a depolarizer.

All natural waters are more or less corrosive, even pure water is corrosive due probably to the tendency of water to satisfy its solvent action.

### PRIMING AND FOAMING.

On this subject Christie says:

"A boiler is said to prime when water is carried as steam bubbles with the steam up through the water to its surface. Foaming is the result of suspended impurities in the water which rise to its surface in a more or less dirty condition and forms a scum.

These conditions are brought about by the presence of considerable quantities of soluble salts such as Sodium chloride, Sodium sulphate and Sodium carbonate which increase the surface tension of water and from finely suspended material as Calcium carbonate and Calcium sulphate disintegrated from the scale in the boiler.

Carney\* says foaming is caused by interference with the free escape of steam from the water of the boiler. He gives as causes: Sodium salts, mud or suspended matter and organic matter.

---

\*A. Inst. Min. Engr's. 1897.

---

In the opinion of C. Herschel Koyl \* foaming is not due

---

\*Railroad Gazette. Oct. 12, 1900.

---





so much to the presence of salts of sodium but rather to the presence of salts of sodium but rather to the presence of suspended solid matter. He found by actual experience that the addition of several hundred grains per gallon of sodium carbonate to distilled water produced no foaming but on the other hand when Calcium carbonate in the form of a fine powder was introduced into boiling distilled water it foamed vigorously.

Salts of sodium are commonly found in natural water but not in quantities great enough to be seriously considered. It is in water treated to remove permanent hardness that their quantity becomes of importance. The following example will illustrate this point:

Laboratory No. 19102

NaCl	45.
MgSO <sub>4</sub>	190.
MgCO <sub>3</sub>	38.
CaCO <sub>3</sub>	236.
FeCO <sub>3</sub>	1.
Al <sub>2</sub> O <sub>3</sub>	3.
SiO <sub>2</sub>	<u>18.</u>
	531.

This water has only 45 parts per million of sodium salts before treatment. After treatment this will have been increased to 315 parts per million.

Christie\* gives the following figures relative to

---

\* Boiler Waters. p. 119.

---



maximum of sodium salts allowable for the different types of boilers without causing foaming:

"Ordinary horizontal boiler 500 to 600 grains per gallon of sodium sulphate.

"Modern water tube boiler 300 to 400 grains per gallon.

"Locomotive boiler 150 to 200 grains per gallon."

Stabler\* has deducted this formula to determine the

---

\*Stabler. Eng. News. Vol. 60, 1908,

---

number of hours a boiler may run under ordinary load without danger of foaming.

$$\text{Run in hours} = \frac{a(c - 1)}{b(f)}$$

Where "a" is the water capacity of the boiler, "b" the hourly quantity of feed water used, "f" is the foaming coefficient and "c" is a constant which represents in parts per million the concentration of salts that will cause excessive foaming in the type of boiler under consideration. The foaming coefficient "f" =  $2.7 \text{ Na} + 2\text{K}$ .

#### LAUNDRIES.

The cleansing value of soap depends on its ability to form suds. No suds will form until all the calcium, magnesium and iron present in the water has combined with the soap to form insoluble oleates or stearates. This curdy soap of these metals is not only a waste of soap, but a decided disadvantage as it deposits on the fibers of the goods, finally appearing as greasy spots on the laundered material.





Iron is especially undesirable in a water used for laundry as it not only consumes soap, but tends to stain any white goods when present even in relatively small quantities.

Whipple\* finds in his experiments that one pound of soap

---

\*The Value of Pure Water. 1907. p. 24.

---

will soften 167 gallon of water having a hardness of 20 parts per million. This is equivalent to 5990 pounds per million gallon. At 5¢ a pound this would amount to about \$3.00 per million gallon.

#### BLEACHING AND DYING.

In bleaching and dying it is first necessary to have the goods thoroughly clean. Where soap curds are deposited upon the goods to be bleached, Prof. Gardner says, "It is impossible to get a thorough bleaching. In the case of some dyestuffs the lime soaps act as a resist, preventing the fixation of the dye and thereby causing light colored or white spots."

#### LEATHER MAKING.

In the tanning industries water is used for the extraction of tannin. If calcium and magnesium are present they will be precipitated as tannates and the tannin rendered useless.

Water is used for washing out the lime used in dehairing the hides. If carbonates of calcium or magnesium are present they will be precipitated in the pores of the hides counteracting the action of tannin and otherwise interfering with dyeing.



### PAPER MAKING.

"Paper and pulp mills require water free from iron which causes rust spots and form calcium and magnesium salts which decompose part of the resin soap used for sizing, requiring more to be used and interfering with the action of coloring matter and the securing of a bright, clear surface.

### ICE MANUFACTURE.

In the making of artificial ice distilled water is mostly used in order to get a pure product. The advantages of pure or softened water is at once evident. Water also serves another purpose in this industry. The compressed gaseous ammonia in cooling gives off a large quantity of heat. Water is used to absorb this heat either by surrounding the ammonia coils with water or sprinkling the water upon the coils. If the water used contains incrusting matter it will be deposited on the hot coils in the form of scale similar to scales in a boiler. This scale tends to greatly decrease the cooling effect of the water.

### WATER TREATMENT.

Water is treated for the purpose of eliminating as far as possible those constituents which make a water less desirable for boiler feeding and other industrial processes. These constituents are the salts of calcium, Magnesium, iron, alumina, carbon dioxide and free hydrochloric acid and sulphuric acid are sometimes present.

For the purpose of comparison water may be divided into



three classes according as they contain sodium carbonate, calcium and magnesium sulphate and magnesium chloride -- Calculated from the ions according to the scheme used in the laboratory of the Illinois State Water Survey.

As an example of Class I we give the following analysis made in the Laboratory of the Illinois State Water Survey:

Laboratory No. 19169.

IONS		HYPOTHETICAL COMBINATIONS	
K	5.0	KCl	9.5
Na	43.0	NaCl	20.6
NH <sub>4</sub>	5.0	Na <sub>2</sub> CO <sub>3</sub>	80.3
Mg	33.5	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	13.5
Ca	73.8	MgCO <sub>3</sub>	116.0
Fe	4.	CaCO <sub>3</sub>	184.2
Al <sub>2</sub> O <sub>3</sub>	4.4	FeCO <sub>3</sub>	8.3
Cl	17.0	Al <sub>2</sub> O <sub>3</sub>	4.4
SiO <sub>2</sub>	14.0	SiO <sub>2</sub>	<u>14.0</u>
			451.8

The most important constituents of this water are the carbonates of sodium, ammonium, magnesium, calcium and iron. This water will not form a hard scale only a soft sludge which may be easily blown off. The hardness of this water is about 330 parts per million as calcium carbonate. According to Whipple's data the cost of soap wasted in using this water in the household and laundry amounts to about \$300 per million gallons.

This water requires only the addition of lime in order to





soften it.

Example of Class II.

Laboratory No. 20283

IONS		HYPOTHETICAL COMBINATIONS	
K	14.	NaNO <sub>3</sub>	.2
Mg	34.6	NaCl	13.2
Ca	77.6	Na <sub>2</sub> SO <sub>4</sub>	25.6
Fe <sub>2</sub> O <sub>3</sub>		MgSO <sub>4</sub>	44.8
	4.9	MgCO <sub>3</sub>	88.8
Al <sub>2</sub> O <sub>3</sub>		CaCO <sub>3</sub>	193.7
NO <sub>3</sub>	.1	Fe <sub>2</sub> O <sub>3</sub>	4.9
Cl	8.0	SiO <sub>2</sub>	<u>29.3</u>
SO <sub>4</sub>	53.6		400.5
SiO <sub>2</sub>	29.3		

This water has about the same soap destroying power as example under Class I. It has, however, tendency to form a hard scale. Both soda and lime must be used in softening this water.

Example Class III:

Laboratory No. 18750

IONS		HYPOTHETICAL COMBINATIONS	
K	5.4	KNO <sub>3</sub>	14.0
Na	21.5	NaNO <sub>3</sub>	36.8
Mg	33.3	NaCl	29.2
Ca	100.1	MgCl <sub>2</sub>	16.5
Fe	.2	MgSO <sub>4</sub>	46.8



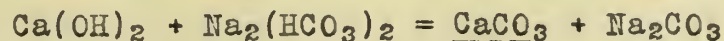
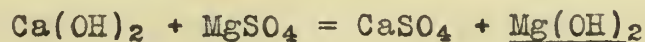
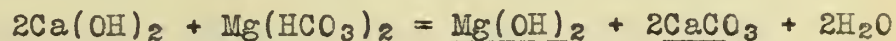
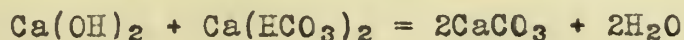
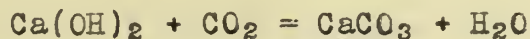
Al <sub>2</sub> O <sub>3</sub>	12.6	MgCO <sub>3</sub>	68.0
NO <sub>3</sub>	35.4	CaCO <sub>3</sub>	250.0
Cl	30.	FeCO <sub>3</sub>	.2
SO <sub>4</sub>	37.3	Al <sub>2</sub> O <sub>3</sub>	12.6
SiO <sub>2</sub>	15.6	SiO <sub>2</sub>	<u>15.6</u>
			489.7

This water has about the same hardness as examples under Class I and II. It is, however, less desirable because magnesium chloride is present which makes this water corrosive. Both lime and soda are required to completely soften it.

As already stated lime and soda are the most practical reagents at the present time for softening purposes because they are the most economical.

Lime reacts with free carbon dioxide, bicarbonates of calcium, magnesium and alkalies and with sulphate and chloride of magnesium. Lime reacts also with salts of iron and aluminium. These elements are seldom present in quantities large enough to come into consideration.

The reactions for lime are:

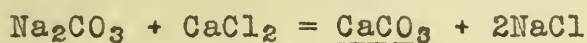


Lime precipitates magnesium as an insoluble hydrate from





whatever combination it may happen to be found in water. But, as may be noted in the above reaction, the corresponding calcium salt is formed which is even less desirable than the magnesium salt. Practically, therefore, soda is added to precipitate the calcium in combination with chlorine and the sulphate radicle. The reactions with soda are as follows:



The compounds underlined are insoluble and fall down as a sludge.

To carry out the process of water softening special apparatus is required. Two general types of softening plants are in use at the present time. The intermittent and the continuous. While the chemical reactions involved in either type are the same, the mechanical devices for accomplishing the thorough softening and purification vary in the different types and with manufacturers of the same type.

The elements necessary to produce a satisfactory soft water are: Definite quantities of reagents, thorough mixing of reagents with the water to be softened, time necessary to complete the reactions and to allow the precipitate to settle.

The simplest form of intermittent softening plant consists of two tanks each holding as much water as will be consumed while the softening process is in progress in the other tank. To the tank containing the raw water is added the calculated amounts of reagents. Lime in the form of milk of lime and soda in the form of a concentrated solution. The stirring is accomplished



by means of paddles mechanically operated and located in the bottom of the tank. These are started as soon as the reagents have been added and continued for some time. After thorough mixing the agitation is discontinued and the water allowed to come to rest. The reaction is complete after about six hours and the precipitate partly subsided. The clear liquid is then drawn off by means of a floating discharge pipe into the storage tank. When the reaction tank is empty it is refilled with raw water and the operation repeated.

Considerable sludge will collect at the bottom of the reaction tank which must be drawn off from time to time. Some deposit, however, should be left and stirred up with the water as it hastens sedimentation.

Calcium carbonate and magnesium hydrate settles very slowly in the cold, about 2.5 inches per hour according to Prof. Wanklyn. To reduce the time element is the object of the continuous type of softeners.

One way to accomplish this is to reduce the distance through which the precipitation has to fall. This is the principal upon which the continuous types are built. It is accomplished by superposing tanks or inclined shilves which catch the precipitate and allow the softened water to be drawn off without disturbing the sludge.

In this system the raw water is split into two streams, one stream is conducted to the bottom of a tank containing lime where it becomes saturated. It then passes on into the mixer where it unites with the main stream. At this point is added the





proportional amount of a solution of sodium carbonate of known strength. From the mixer the water passes down to the bottom of the main tank and slowly passes upwards depositing sludge on the enclined shelves. The softened water is drawn off at the top and filtered upwards thru excelsior.

The amount of caustic lime taken up by water is a constant quantity for any given temperature--91 grains per gallon at 15°C. For waters having a fixed quantity of dissolved solids, the required lime addition can be regulated to a considerable degree of accuracy. With surface waters which are variable as to the amount of dissolved material this type of softeners are not entirely satisfactory.

Another method of softening water is to utilize the exhaust steam or flue gases for heating the water up to the boiling point before it enters the boiler. At this temperature the bicarbonates are changed to normal carbonates. Sometimes soda is added to change the chlorides and sulphates of calcium and magnesium to carbonates.

#### ANALYSIS AND CONTROL.

The object of water softening is to remove as far as possible those constituents in water which cause hardness, without leaving an excess of reagents in the treated water. This is a comparatively easy problem in the case of ground waters where the constituents do not vary appreciably from time to time. It is, however, a more serious matter where surface water is used which may not show the same amount of dissolved material on two successive occasions.





The determination of the amount of reagents to be added to a water may be effected in several different ways. A logical method of accomplishing this would be to treat a series of samples with varying amounts of the reagent and analyzing the filtrate after the completion of the reaction. This, however, is not practical.

The most accurate method is to make a complete mineral analysis. This involves the determination of sodium, ammonium, magnesium, calcium, iron, alumina, nitrate, chlorine, sulphate, carbonate and silica. By combining these ions, in the order in which they are given, into hypothetical combinations the amount of reagents to be added may be calculated from these combinations by the use of proper factors.

There are differences of opinion among authorities as to whether combinations into salts should be made. R. B. Dole\* says,

---

\*Water Supply Paper No. 236. p. 40.

---

though salts are probably present in solution the analytical data is insufficient to permit the apportionment of the bases among the acids. F. W. Clarke\* says, with reference to hypothetical combi-

---

\*Bull. U. S. Geol. Survey No. 330, 1908. p. 54.

---

nation, "The result is a meaningless chaos of assumptions and uncertainties." E. G. Bashore\* presupposes hypothetical combina-

---

\*M. & C. E. Vol. VIII, No. 1. p. 20.

---

tions when he says, "Each grain of calcium and magnesium bicarbonate reported in the analysis as carbonates," etc. In the Labo-



ratory of the Illinois State Water Survey combinations are generally made.

In examining water for industrial purposes these combinations are not in the least misleading, but on the other hand show at glance whether a water will form hard or soft scale, cause corrosion or foaming. While it is true that they are not necessary for the determination of reagents required, they serve admirably for the purpose for which they were intended.

Stabler\* has deduced a very ingenious formula for deter-

---

\*Engineering News, vol. 60, 1908, p. 355.

---

mining the amount of lime and soda from the ions in terms of 90% lime and 95% soda per 1000 gallons.

Lime required =  $.26(rFe + rAl_3rMg + rH + rHCO_3 + .0454CO_2)$

Soda ash required =  $.465(rFe + rAl + rCa + rMg + rH - rCO_2 - rHCO_3)$ .

"r" is a constant for each element and is the ratio between the valance and the molecular weight of the elements.

We believe that the above formula may be greatly simplified by writing

Lime =  $.0052 (4.16 Mg + Alk + CO_2)$  lbs. per 1000 gal. of 90% tin

Soda ash =  $.0093 (4.16 Mg + 2.5 Ca - Alk)$  lbs. per 1000 gal. of 95%  $Na_2CO_3$ .

Iron and aluminium are not figured in the above formula because they are generally low. However, if iron is present as a carbonate it is included in alkalinity.  $HCO_3$  and  $CO_2$  are generally determined by titration, the former by means of a standard acid and the latter by a standard  $Na_2CO_2$  solution. The error, therefore, will be the same in both formulas.





E. G. Bashore\* calculates the lime required by dividing

---

\*M. & C. E. Vol. VIII, No. 1, p. 20.

---

each grain of calcium and magnesium bicarbonate reported in the analysis as carbonate by 5.5. This statement is false in principal because magnesium is not precipitated as a carbonate but as a hydrate. He calculates soda by dividing the number of grains per gallon of magnesium sulphate by 8 and the number of grains of calcium sulphate by 8.75. The quotient represents pounds per 1000 gallons.

To show that the same results are obtained by calculating the lime and soda requirement according to the methods already suggested, analysis No. 20578 has been calculated according to Stabler's formula, simplified formula and hypothetical combinations.

IONS		HYPOTHETICAL COMBINATIONS	
Na	52.	NaCl	41.
Mg	24.3	Na <sub>2</sub> SO <sub>4</sub>	112.
Ca	66.8	MgSO <sub>4</sub>	76.4
Fe	.2	MgCO <sub>3</sub>	32.6
Al <sub>2</sub> O <sub>3</sub>	1.8	CaCO <sub>3</sub>	167.0
Cl	25.0	FeCO <sub>3</sub>	.4
SO <sub>4</sub>	137.0	Al <sub>2</sub> O <sub>3</sub>	1.8
SiO <sub>2</sub>	18.7	SiO <sub>2</sub>	<u>18.7</u>
			449.9



Stabler's formula,

$$\text{Lime} = .26(.0333 \times 123.6 + .0821 \times 24.3) = 1.58$$

Simplified formula,

$$\text{Lime} = .0052(4.16 \times 24.3 + 206) = 1.58$$

Hypothetical combinations,

$$\text{MgSO}_4 \quad 76.5 \times .46 = 35.2$$

$$\text{MgCO}_3 \quad 32.6 \times 1.33 = 43.3$$

$$\text{CaCO}_3 \quad 167. \times .56 = \underline{93.5}$$

Total lime in parts per M. 172.0

$$90\% \text{ lime per 1000 gallons } .0092 \times 172 = 1.58$$

Stillman\* has proposed a scheme for the rapid analysis of boiler waters which is an improvement over the complete mineral analysis in this that it consumes less time. It is also fairly accurate. The desired amount of water is evaporated and weighed, this gives total solid. It is then ignited, weighed, and moistened with water and placed in atmosphere of  $\text{CO}_2$  and weighed. The last operation gives total mineral matter. The non scale forming ingredients are separated from the scale forming by extraction with 50 c.c. of distilled water, filtered and the residue treated with HCl and  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , Ca, Mg, and  $\text{SO}_4$  determined gravimetrically.

---

\*Engineering Chemistry, Second Edition, p. 53.

---

The methods mentioned so far are accurate but they have the disadvantage of requiring a lot of time, beside considerable manipulation skill.

The need for a method which is rapid, fairly accurate and



in which the apparatus and reagents used are reduced to a minimum is apparent. This method must show clearly the character of the water and present the data in such a form that the amount of reagent to be added may be readily calculated.

With the object in view of finding such a method the literature on the subject was searched. A number of methods were found. Each one, however, failed in one or more important details to satisfy the above conditions.

The simplest of these methods is due Dr. Dudley, former chemist of the Pennsylvania Railroad. He treats the residue on evaporation with 70% alcohol and calls the insoluble residue scale-forming. This treatment gives nothing more than the total hardness. It is, however, of value as a substitute for the soap test.

A. Elliott Kimberly\* proposes a method for the rapid

---

\*Journal of Infectious Diseases. Supp. May 1905, p. 157.

---

analysis for water softening. He says, "To calculate the chemicals necessary for the treatment of a magnesium water, the following data is necessary:

1. Free and half bound carbonic acid
2. Alkalinity
3. Incrustants
4. Total magnesium
5. Total calcium
6. Incrusting calcium

Numbers 1, 2, 3 and 4 are determined according to Standard Methods. Total calcium is calculated by deducting total magnesium





as calcium carbonate from total hardness as calcium carbonate. Incrusting calcium is determined by boiling 500 c.c. to 200 c.c., filtering and Ca determined gravimetrically from the filtrate. An allowance is made for the solubility of normal  $\text{CaCO}_3$  which is taken as 20 parts per million. .

From the data thus obtained he calculates the component bases of alkalinity and incrustants.

Alkalinity. That quantity of calcium present as an incrustant is subtracted from the total calcium. The remaining calcium may be attributed to alkalinity. The difference between alkalinity determined by titration and that portion due to calcium must be the magnesium component of alkalinity.

Incrustants. Calcium is determined directly as described above. The difference between total magnesium and that attributed to alkalinity gives incrusting magnesium.

He gives the following data obtained from an analysis by the above scheme:

Constituents expressed in parts per million.

		as $\text{CaCO}_3$
Alkalinity as $\text{CaCO}_3$	252,	252.
Total Incrustants as $\text{CaCO}_3$	174.	174.
Total magnesium as Mg	44.	182.
Total calcium as Ca	98.	244.
Incrusting calcium as Ca	25.	63.

Calculation of lime required to soften above water.

	as $\text{CaCO}_3$	
Alkalinity (Ca	183 x .56 = lime required =	102
(Mg	70 x 1.12 = lime required =	77
Incrusting Mg	112 x .56 = lime required =	63
	Total lime	242



Calculation of Sodium Carbonate required to soften above water.

(Ca	62 x 1.06 = Na <sub>2</sub> CO <sub>3</sub> required =	65.
Inc. (		
(Mg	112 x 1.06 = Na <sub>2</sub> CO <sub>3</sub> required =	<u>119.</u>
	Total Soda	184.

By means of a very simple formulae identical results may be obtained using only three of Mr. Kimberly's data.

Data required	Parts per million as CaCO <sub>3</sub>
Incrustants	174.
Total Mg.	182.
Alkalinity	252.

Formulae:

.56 (Mg + Alk.) = lime required

1.06 x Incrustants = Na<sub>2</sub>CO<sub>3</sub> required

From above consideration it is obvious that the determination of total calcium and incrusting calcium is superfluous. It does not throw any additional light on the character of the water.

It is Mr. Kimberly's contention that above method of analysis is especially adapted to magnesia waters --waters Containing large amounts of magnesium.

To test this method an analysis was made on a water having the following composition:

	Laboratory No. 20283
	Parts per million
NaCl	13.0
Na <sub>2</sub> SO <sub>4</sub>	26.0
MgSO <sub>4</sub>	45.0
MgCO <sub>3</sub>	89.0





CaCO <sub>3</sub>	194.0
Fe <sub>2</sub> O <sub>3</sub>	5.0
SiO <sub>2</sub>	29.0

1000 c.c. of the water was concentrated to 300 c.c. filtered and calcium determined gravimetrically by precipitation with ammonium oxalate. The other data was determined as directed in Kimberly's article.

Alkalinity as CaCO <sub>3</sub>	283.0
Total incrustants as CaCO <sub>3</sub>	40.0
Total magnesium	126.0
Total calcium	177.0
Incrusting calcium	0.0

The amount of calcium found in the filtrate after concentrating a liter to 300 was 16.0 parts per million which is well within the solubility limit of calcium carbonate. In this case, therefore, no incrusting calcium was present.

According to an article in the Chemical Engineer\* the

---

\*Anon. Chemical Engineer. Vol. XI. No. 2. Feb. 1910.

---

following methods are used by the Pittsburg Testing Laboratories, J. O. Handy, Chief Chemist:

Method I. 250 c.c. are evaporated and total residue determined. This residue is treated with CO<sub>2</sub> free distilled water and filtered. The filtrate contains all the alkalie salts together with the sulphates and chlorides of iron, aluminium, calcium and magnesium. The insoluble residue consists of carbonates of lime and magnesium with some silica. The soluble and insoluble portions are



analyzed separately. Alkalies are determined indirectly. The insoluble carbonates are dissolved in dilute HCl. The iron is precipitated with  $\text{NH}_4\text{OH}$  dissolved in dilute  $\text{H}_2\text{SO}_4$  and titrated with standard  $\text{KMnO}_4$  solution after reduction with zinc. Calcium is precipitated with ammonium oxalate dissolved in hot 2% solution  $\text{H}_2\text{SO}_4$  and titrated with  $\text{KMnO}_4$ . The magnesium is precipitated by the addition of a phosphate and  $\text{NH}_4\text{OH}$ . The precipitate is dried, dissolved in  $\text{H}_2\text{SO}_4$  and the excess titrated back with N/10 NaOH. The insoluble part is acidified with HCl and the iron, calcium and magnesium determined as above.

Chlorine is determined by titrating 100 c.c. with standard  $\text{AgNO}_3$  using  $\text{KCrO}_4$  as indicator.

Sulphuric anhydride is determined in a separate portion as  $\text{BaSO}_4$ .

Nitric anhydride is determined by the phenol-sulphonic acid method.

Alkalinity is determined by titrating 100 c.c. with  $\text{H}_2\text{SO}_4$ .

Acidity is determined by adding to 100 c.c. a measured amount of N/10  $\text{H}_2\text{SO}_4$  boiled to drive off  $\text{CO}_2$  and titrated back with N/10 NaOH.

Free  $\text{CO}_2$  is determined by Seyler's method.

Silica is determined in a separate portion in the usual manner.

Bases and acids are combined by calculating the insoluble iron, calcium and magnesium to carbonates. If the sum is less than alkalinity the difference is  $\text{Na}_2\text{CO}_3$ . The soluble iron, aluminium, calcium and magnesium are calculated to first sulphate then nitrate



and finally to chlorides. The residual acid radicals are calculated to sodium salts.

The chemicals required for softening is determined by calculating,

One equivalent of lime for one equivalent insoluble Ca								
Two	"	"	"	"	"	"	"	Mg
One	"	"	"	"	"	"	"	soluble Mg
"	"	"	"	"	"	"	"	free acid
"	"	"	"	"	"	"	"	insoluble Fe
"	"	"	soda ash for one equivalent soluble Ca					
"	"	"	"	"	"	"	"	Mg
"	"	"	"	"	"	"	"	free H <sub>2</sub> SO <sub>4</sub>

While the method of analysis and calculation of chemicals required is correct, it has no advantage over the complete mineral analysis.

Method II. A peculiar inconsistency is here noticed where the author says, "The tests necessary for calculating treatment of hard water are:

1. Hardness

2. Alkalinity

3. Acidity (free CO<sub>2</sub>)

Hardness is determined by titrating 100 c.c. with N/10 soap solution.

Alkalinity is determined by titrating 100 c.c. with N/50 H<sub>2</sub>SO<sub>4</sub> using methyl orange as indicator.

Acidity is determined by titrating 200 c.c. with N/50 NaOH<sub>4</sub> using phenolphthalein as indicator.





Calculations are made as follows:

Lime. Alkalinity + Acidity x .056 lbs. = lime required for 1000 gallon of water.

Soda Ash. Hardness-Alkalinity x .093 lb. = soda ash required for 1000 gallons.

This is inconsistent with Method I and is evidently erroneous, as it does not take into account that lime reacts with magnesium present as incrustant nor that magnesium present as bicarbonate must be precipitated as a hydrate.

A comparison will show this more clearly,

#### METHOD I.

Laboratory No. 20283

Parts per 1000,000		Pounds per U. S. gallon	
		Commerical lime 90% needed	
CaO (insoluble)	10.8 x .0925 =	.999	
MgO (insoluble)	4.2 x .26 =	1.094	
MgO (soluble)	1.5 x .13 =	<u>.195</u>	
Total		2.288 lbs.	

CaO (soluble)	0.	Soda ash 95%	
		Na <sub>2</sub> CO <sub>3</sub> needed	
MgO (soluble)	1.5 x .233 =	.34	

#### METHOD II.

Laboratory No, 20283

<u>Lime</u>		Parts per		Pounds	
Alkalinity + Acidity		100,000		per 1000	
		as CaCO <sub>3</sub>		gallons	
30.0	+ 0 =	30.0 x .056	=	1.68	



Soda Ash

Hardness - Alkalinity

$$33.7 - 30.0 = 3.7 \times .093 = .34$$

As would be expected the total lime required is entirely too low as determined by Method II.

Using the same data as in Method I the total lime and soda required may be determined by the simple formulae,

$$\begin{aligned} \text{Lime required} &= .0052 (\text{Mg} + \text{Alk}) \\ &\text{Lbs. per 1000 gal.} \\ &\text{90\% lime} \\ (143 + 300) .0052 &= 2.3 \end{aligned}$$

$$\begin{aligned} \text{Incrustants} \times .0098 &= \text{Soda Ash required} \\ &\text{Lbs. per 1000 gal.} \\ &\text{95\% Na}_2\text{CO}_3 \end{aligned}$$

$$.37 \times .0098 = .34$$

N.B. Mg equals MgO soluble and insoluble as  $\text{CaCO}_3$

Incrustants equals soluble CaO plus soluble MgO as  $\text{CaCO}_3$ .

A rapid method for the control of water softening depending on the use of potassium stearate has been proposed by Von C.

Blacher, U. Koerber and J. Jacoby.\* The following constituents are

---

\*Zeit. fur Angwt. Chem.

---

determined:

1. Alkalinity
2. Total hardness
3. Calcium hardness
4. Sulphuric acid
5. Total Bases.





The reagents required are: N/10 HCl, N/10 BaCl<sub>2</sub> and N/10 potassium stearate. The potassium stearate solution is prepared by dissolving 28.4 grams pure stearic acid in 250 grams glycerine and 400 c.c. 90% alcohol, warming gently. This is neutralized to phenolphthalein with alcoholic KOH and made up to a liter with 90% alcohol.

Alkalinity is determined by titrating 100 c.c. of the water with N.10 HCl using methyl orange as an indicator.

Total hardness is determined by acidifying 100 c.c. of water boiled to drive off CO<sub>2</sub>. It is cooled and brought to the exact phenolphthalein neutral point. All or an aliquot portion is then titrated with potassium stearate.

Calcium hardness is determined by acidifying 100 c.c. to the methyl orange neutral point. Air is passed through to drive off CO<sub>2</sub>. This is rinsed into a 110 c.c. flask. For the precipitation of magnesium 1:1 alcohol and KOH is added. The flask is placed on the steam bath until the precipitate has coagulated, filtered warm and 100 c.c. of the filtrate withdrawn for the determination of calcium hardness. This is acidified and boiled down to 30 or 40 c.c. and titrated with potassium.

Sulphuric acid is determined by acidifying 100 c.c. of the water and adding 5.10 or 15 c.c. of N/10 BaCl<sub>2</sub> to the boiling solution and concentrated to 10 c.c. The precipitate is filtered off and the neutral point is fixed to phenolphthalein. The excess of BaCl<sub>2</sub> is determined by titrating with potassium stearate.

Total bases are determined by evaporating to dryness 100 c.c. of the water. A few drops of H<sub>2</sub>SO<sub>4</sub> is added and heated



over a flame to drive off organic matter and excess  $\text{H}_2\text{SO}_4$ . Sulphate is then determined as above.

This method depends for the end-point on the formation of a lather and like the soap test it is not reliable. Standard Methods has this to say about the soap method: "At best the soap method is not a precise test on account of the varying amounts of calcium and magnesium present in different waters. For hard waters, especially in connection with processes for purification and softening, it is advised that this method be not used."

In the determination of alkalinity a weaker acid should be used, say N/50.

In Technical Methods of Chemical Analysis, Part II, p.802, Lunge proposes these special tests to determine the amounts of lime and sodium carbonate necessary for the treatment of water:

1. Clear lime water, previously titrated with N/5 HCl, using phenolphthalein as indicator, is added to 200 c.c. of the water under examination until the first coloration appears and remains for a short time. This test indicates the amount of lime which must be added.

2. The turbid liquid obtained according to 1 is filtered, the filtrate treated with an excess of alkali titrated back with N/5 HCl.

P. Bilger\* has modified the above method somewhat. He

---

\*Chem. Zeit. 33. p. 757.

---

adds 30 c.c. of lime water to 100 c.c. of the sample, heats to boiling. When cool the volume is made up to 200 c.c. with  $\text{CO}_2$  distilled



water and allowed to settle. 100 c.c. of the clear liquid is then withdrawn and titrated with N/10 HCl using phenolphthalein as indicator.

### EXPERIMENTAL

The following experimental work was undertaken for the purpose of testing the adaptability for the control of water softening of the methods already outlined. If possible, also, to devise new methods or combine methods already in use so as to make a method which is at the same time rapid, accurate and complete.

For this purpose water from the city supply of Belleville, Illinois was selected because it is a representative sample of a hard water requiring both lime and soda ash to soften it.

A complete mineral analysis was first made. The procedure was as follows:

Two portions of 1000 c.c. each was evaporated to dryness with HCl, heated in the oven at 180° for an hour to dehydrate the silica, moistened with HCl and about 40 c.c. of water added. This was then heated on the steam bath until all was in solution. The silica was filtered off and washed with hot water. The residue was incinerated in a weighed platinum crucible and weighed as silicious matter. In one portion was determined iron and alumina, calcium and magnesium; in the other sulphate and the alkalies.

Iron was determined by oxidizing the filtrate from silica with 1 c.c.  $\text{HNO}_3$  the solution was made alkaline with  $\text{NH}_4\text{OH}$  and acidified with HCl and finally a slight excess of ammonia was added,





the excess boiled off, filtered and washed.

The precipitate was ignited and weighed as combined oxides of iron and alumina. The filtrate from the iron was heated to boiling and crystals of ammonium oxalate was added in excess. The calcium oxalate was filtered off, ignited, washed and weighed as  $\text{CaO}$ . The filtrate from the calcium determination was acidified with  $\text{HCl}$ , 40 c.c. saturated solution of sodium ammonium acid phosphate was added and boiled for five minutes, cooled quickly and  $\text{NH}_4\text{OH}$  in slight excess. After standing 12 hours the precipitate was filtered off and washed with water containing 3%  $\text{NH}_4\text{OH}$ . The precipitate was ignited in a porcelain crucible and weighed as  $\text{Mg}_2\text{P}_2\text{O}$ .

The filtrate from the second portion of silica was heated to boiling. Ten cubic centimeters of a 10% solution of  $\text{BaCl}_2$  was added and allowed to stand on the hot plate for about 30 minutes, filtered and washed thoroughly with hot water. The precipitate was ignited and weighed as  $\text{BaSO}_4$ .

The filtrate was evaporated to dryness, taken up with a little water,  $\text{Ba}(\text{OH})_2$  added to precipitate the magnesium, filtered and washed. The filtrate was treated with  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{NH}_4\text{OH}$  to precipitate calcium and excess of  $\text{Ba}(\text{OH})_2$ , filtered and the filtrate evaporated to dryness and the ammonium salts driven off by heating almost to the melting point of the alkalies. This operation was repeated until the addition of  $(\text{NH}_4)_2\text{CO}_3$  gave no precipitate. The combined alkalies were weighed as  $\text{NaCl}$ .

The following results were obtained by the above method:

Ions in parts per mil.

Hypothetical combinations  
in parts per mil.

Na 13.9

$\text{NaNO}_3$  .2



NH <sub>4</sub>	.5	NaCl	13.2
Mg	34.6	Na <sub>2</sub> SO <sub>4</sub>	26.5
Ca	77.6	MgSO <sub>4</sub>	44.8
Fe <sub>2</sub> O <sub>3</sub> +		MgCO <sub>3</sub>	88.8
Al <sub>2</sub> O <sub>3</sub>	4.9	CaCO <sub>3</sub>	193.7
NO <sub>3</sub>	.1	Fe <sub>2</sub> O <sub>3</sub> +	
Cl	8.0	Al <sub>2</sub> O <sub>3</sub>	4.9
SO <sub>4</sub>	53.6	SiO <sub>2</sub>	<u>29.3</u>
SiO <sub>2</sub>	29.3		401.2

Residue on evaporation 410.

Alkalinity 283.

The same water was analyzed by the rapid method suggested by Wartha and Pfeifer with slight modifications. The procedure followed was as follows:

Mineral Acid Hardness--200 c.c. of the water was placed in a 500 c.c. Jena Erlenmeyer flask, boiled for fifteen minutes to drive off all the CO<sub>2</sub>. Twenty-five cubic centimeters N/10 mixture of equal parts of Na<sub>2</sub>CO<sub>3</sub> and NaOH was added. After boiling to a volume of about 100 c.c. the liquid was filtered and made up to 200 c.c. with CO<sub>2</sub> free distilled water. A blank was treated in exactly the same way. Fifty cubic centimeters of the clear solution was titrated with N/50 H<sub>2</sub>SO<sub>4</sub> using methyl orange as indicator. The difference between blank and sample x 20 equals mineral acid hardness as CaCO<sub>3</sub>.

Total Magnesium--200 c.c. of the water was made neutral to methyl orange with N/10 NCl, boiled for 15 minutes. Fifty cubic centimeters of saturated lime water was added. After cooling the





liquid was filtered and made up to 200 c.c. with CO<sub>2</sub> free distilled water. A blank was treated exactly as the sample. Fifty cubic centimeters of the filtrate was withdrawn and titrated with N/50 H<sub>2</sub>SO<sub>4</sub> using methyl orange as indicator.

Blank reading - sample reading x 20. = parts per million  
of magnesium as CaCO<sub>3</sub>.

The following data were obtained by above method:

	Parts per million as CaCO <sub>3</sub>
Mineral Acid Hardness	40.0
Total Magnesium	136.0
Alkalinity	283.0

The class of water to which a sample belongs may be readily ascertained by an inspection of the data as obtained in terms of CaCO<sub>3</sub>. For example, in the above analysis the Mineral Acid Hardness is less than total magnesium. Therefore, we say part of the magnesium is present as a sulphate and the remainder as bicarbonate. If in an analysis, the Mineral Acid hardness is greater than total magnesium we know that part of the calcium and all of the magnesium is present as a sulphate. If on the other hand, the Mineral Acid Hardness is negative no sulphates of calcium or magnesium can be present.

For the purpose of testing the accuracy of the rapid method just outlined a number of samples were analyzed both by the gravimetric and by the rapid methods. The results appear in the following table:



NUMBER

M E T H O D

	Gravimetric		Rapid Boiler	
	Magnesium Parts per M. as CaCO <sub>3</sub>	Acid Hardness Parts per Million as CaCO <sub>3</sub> .	Magnesium Parts per M. as CaCO <sub>3</sub>	Acid Hardness Parts per Million as CaCO <sub>3</sub>
18754	162	-266	166	-233
19041	1015	2056	1016	2058
20445	111	-5	112	-10
20505	88	-65	84	-86
20283	143	37	136	42
Lena, raw	200	39	192	45
Lena, treated	78	-1	68	0
Mendota, raw	70	-55	66	-48
Mendota, treated	---	-50	40	-48

The above results show that the determinations made by the rapid method agree favorably with the gravimetric determinations. Although there are some differences the method is accurate enough for the control of water softening.

Calculations may now be made from the above data to determine the amount of reagents to be added.

From the rapid analysis we have for lime:

$$\text{Mg} + \text{Alk.} = \text{Lime required as CaCO}_3$$

$$136 + 283 = 419.$$

For soda ash,

$$1.06 \text{ M. A. H} = \text{Soda ash required as Na}_2\text{CO}_3$$

$$1.06 \times 40 = 42.$$

For the purpose of practically testing the above method of calculating the reagents required a series of sixteen liters of Belleville water in sixteen two-liter glass stoppered bottles



was treated with varying amounts of lime of known strength. The bottles were well shaken after the addition of lime and allowed to stand for 14 hours. They were then filtered and alkalinity to phenolphthalein and methyl orange immediately determined. Calcium and magnesium were determined gravimetrically in 250 c.c. of the filtrate. The results appear in Table I.

In another series six liters were used for the purpose of testing method of calculating soda ash. To each of the two liter bottles each containing one liter of water was added varying amounts of sodium carbonate. After standing 14 hours they were filtered and the mineral acid hardness determined as described above. The following results were obtained:

TABLE II.

TREATMENT OF BELLEVILLE WATER WITH $\text{Na}_2\text{CO}_3$ .			
No.	c.c. $\text{Na}_2\text{CO}_3$ solution added	Milli- grams $\text{Na}_2\text{CO}_3$	Mineral Acid Hardness Pts. per Mil. as $\text{CaCO}_3$
1	0	0	42.4
2	20	44	4.0
3	25	55	-4.0
4	30	66	-34.0
5	35	77	-47.0
6	40	88	-60.0

A third series was treated with the same amount of lime as in Series I but 46 mg. of Sodium carbonate was added to each bottle. The results are recorded in Table III.

It will be noticed from these tables and diagrams that





TABLE I.  
TREATMENT OF BELLEVILLE WATER WITH LIME.

No.	c.c. Lime Water	Amt. of Lime Used	Alkalinity to Phenolphthalein	Alkalinity to Methyl Orange	Hardness by Soap Test	Hardness corr. for Vol.	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> in Mg.	CaO in Mg.	Ca in Pts. per Mil.	Mg in Pts. per Mil.
			Corr. for Vol. Pts. per Mil.	Corr. for Vol. Pts. per Mil.	Pts. per Mil.	Pts. per Mil. as CaCO <sub>3</sub>				
1	0	0	0	14.0	---	330	158.5	108.6	77.4	34.5
2	10	20	0	13.7	308	311	---	---	---	---
3	20	40	0	13.0	300	306	153.	84.4	61.5	34.
4	40	80	?	10.1	272	283	---	---	---	---
5	60	120	0	8.9	236	250	150.	64.8	49.1	35.
6	80	160	28	7.6	168	181	---	---	---	---
7	100	200	23	6.0	172	189	141.	35.2	27.7	34.
8	120	240	47	5.7	120	134	---	---	---	---
9	140	280	47	5.1	100	114	117.6	31.6	25.7	29.3
10	160	320	26	3.0	102	118	---	---	---	---
11	180	360	36	2.4	92	108	60.	42.8	36.	15.5
12	200	400	39	2.5	88	105	---	---	---	---
13	220	440	40	2.2	104	126	26.8	57.6	50.2	7.1
14	240	480	63	3.0	116	143	---	---	---	---
15	260	420	104	4.3	148	189	24.0	80.8	74.	6.6
16	280	560	152	6.2	---	---	---	---	---	---
17	300	600	206	8.8	---	---	21.2	159.2	150.	6.2





# Graph Showing Relation Between

Lime Added AND

Alkalinity to Methyl Orange.

" " Phenolphthalein

And to Calcium AND Magnesium

When Lime alone is used

## Legend

--- Alkalinity to Methyl Orange.

--- " " Phenolphthalein

--- Calcium

--- Magnesium.

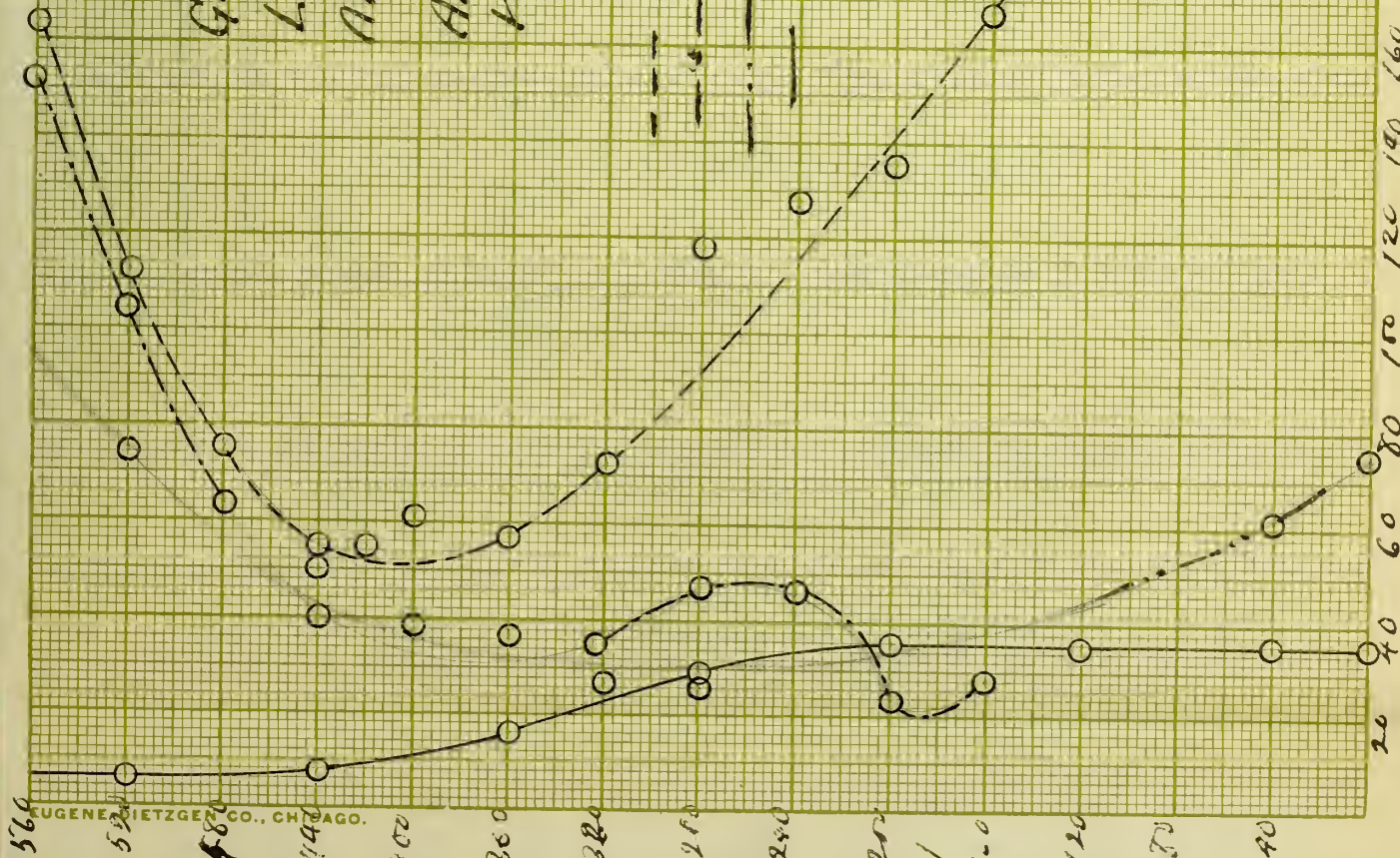








TABLE III.  
TREATMENT OF BELLEVILLE WATER WITH LIME AND SODA.  
42 Milligrams  $\text{Na}_2\text{CO}_3$  added to each liter.

No.	c.c. Lime Water	Amt. of Lime Used	c.c.N/50 $\text{H}_2\text{SO}_4$	c.c.N/50 $\text{H}_2\text{SO}_4$	Alkalinity to Phenolphthalein Corr. for vol.	Filtrate	Alkalinity to Methyl Orange Corr. for vol.	$\text{Mg}_2\text{P}_2\text{O}$ in Mg.	$\text{CaO}$ in Mg.	Ca in Pts. per Mil.	Mg in Pts. per Mil.
1	0	0	0	0	0	0	0	158.5	108.6	77.4	34.5
2	12	21	0	0	0	16.	323	---	---	---	---
3	20	42	0	0	0	14.2	289	158.	56.	40.	34.4
4	40	84	0	0	0	11.8	245	---	---	---	---
5	60	126	0	0	0	9.7	206	---	---	---	---
6	80	168	0	0	0	8.0	173	---	---	---	---
7	100	210	0	0	0	6.7	147	158.	41.	29.	34.4
8	120	252	0	0	0	5.8	130	---	---	---	---
9	140	294	.7	16	0	4.8	107	---	---	---	---
10	160	336	1.0	23	16	4.0	93	132.	16.	13.0	27.
11	180	378	1.2	27	23	3.3	78	---	---	---	---
12	200	420	1.0	24	24	2.2	52	42.	21.	15.	9
13	220	462	1.2	30	30	2.0	49.	---	---	---	---
14	240	504	1.4	35	35	1.9	47.	---	---	---	---
15	260	546	1.5	38	38	2.6	66.	21.	52.	37.	6.





# Graph II Showing Relation Between

Lime added and

Alkalinity to Methyl Orange

" " Phenolphthalein

Acid to Calcipon and Magnesium

When lime and Soda Ash is used.

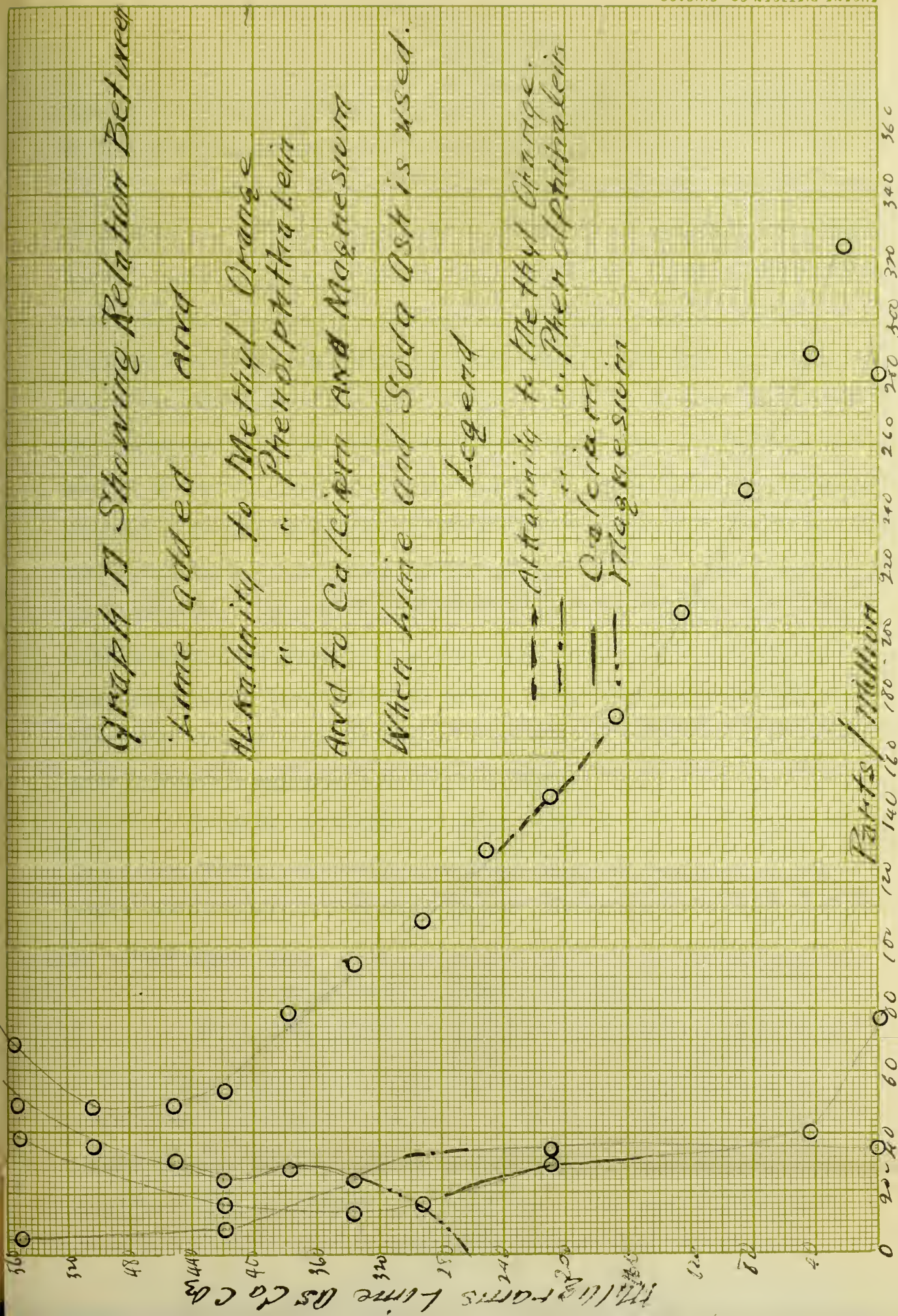
Legend

--- Alkalinity to Methyl Orange.

--- " " Phenolphthalein

--- Calcipon

--- Magnesium







the practical results agree, within the limit of experimental error, with the calculation by above formulae.

A further inspection of Graph I shows the following order of reactions: In all probability free  $\text{CO}_2$ , if present, is attacked first. Calcium bicarbonate is next attacked. This is shown by the simultaneous decrease in alkalinity to methyl orange and the calcium content while the magnesium content remains constant up to the point where 200 milligrams has been added. This is further substantiated by the analysis which shows that 194. milligrams of calcium carbonate is present. From this point up to 280 milligrams of lime there is only a slight reduction in calcium and magnesium. However, when 320 milligrams of lime has been reached alkalinity has been reduced to a minimum. This is evidently the point where lime has reacted with calcium and magnesium present as bicarbonates and is the best treatment where lime alone is used. From this point on magnesium decreases and calcium increases showing that  $\text{MgSO}_4$  is decomposed into insoluble  $\text{Mg}(\text{OH})_2$  and soluble  $\text{CaSO}_4$ .

A study of Graph II shows that the same order of reactions has taken place. The best treatment appears to be at the point where 420 milligrams has been added. This agrees very well with our formulae,

$$\text{Mg} + \text{Alk.} + \text{CO}_2 = \text{lime required.}$$

It was thought that the method proposed by Lunge and modified by Bilger as already described, would afford with some slight modifications a rational and accurate means for the determination of the amount of lime to add to a water. A series of experiments were therefore carried out. The procedure was as





follows:

200 c.c. of the water to be tested was measured off into a 500 c.c. Jena Erlenmeyer flask. 75 c.c. of saturated lime water was immediately added and the volume boiled down to a little below 200 c.c. cooled, filtered and made up to 200 c.c. with CO<sub>2</sub> free distilled water. 50 c.c. was withdrawn and titrated with N/50 H<sub>2</sub>SO<sub>4</sub> using methyl orange as indicator.

A modification of Lunge-Bilger method was also tried. The modification consisted in adding Na<sub>2</sub>CO<sub>3</sub> to the sample in quantity equivalent to the amount of mineral acid hardness. Otherwise the procedure was as above. This method of procedure is an exact duplicate of the practical methods of water softening. Theoretically, therefore, it shows the amount of lime used up in reacting with sulphate of magnesium, bicarbonates of calcium and magnesium, salts of iron and aluminium and free CO<sub>2</sub>.

The strength of the lime water was obtained by running a blank determination similar to the sample except that no Na<sub>2</sub>CO<sub>3</sub> was added. By either method lime required = 20 (Burette reading blank - Burette reading sample) when N/50 acid used.

For the purpose of comparison each sample was analyzed by the rapid boiler method and lime calculated by the formula,

$$\text{Lime required} = \text{Mg} + \text{Alk.} + \text{CO}_2$$

The following are some of the results:

Laboratory No. 20734.

Method	Lime required as CaCO <sub>3</sub>
Rapid Boiler	446
Lunge-Binger	560



Modified Lunge-Bilger	576
-----------------------	-----

Laboratory No. 20741

Rapid Boiler	670
Lunge-Bilger	728
Modified Lunge-Bilger	720

Laboratory No. 20746

Rapid Boiler	440
Lunge-Bilger	474
Modified Lunge-Bilger	460

In a number of other samples similar results were obtained, It will be noticed that the lime required as determined by the use of excess of lime with with or without  $\text{Na}_2\text{CO}_3$  is greater than as determined by the Rapid Boiler method. To further test this method artificial hard waters were made up.

Solution A. To 20 liters of distilled water was added 4 grams  $\text{CaSO}_4$ , 10 grams  $\text{MgSO}_4$ , 7 grams  $\text{H}_2\text{O}$  and 4.6 grams  $\text{CaCO}_3$ . On analysis this water showed:

	Amount found	Amount added
Mg as $\text{CaCO}_3$	188.	196.
Mineral Acid Hardness as $\text{CaCO}_3$	332.	324.
Alkalinity as $\text{CaCO}_3$	230.	230.
Free $\text{CO}_2$ as $\text{CaCO}_3$	10.	10.

Method	Lime required
Rapid Boiler	428.
Lunge-Bilger	526.
Modified Lunge-Bilger	540.





Solution B. To 14 liters was added 7.6 grams  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and 3.8 grams  $\text{CaCO}_3$ . On analysis this water showed:

	Amount found	Amount added
Mg as $\text{CaCO}_3$	230.	220.
Mineral Acid Hardness	200.	220.
Alkalinity	274.	274.
Free $\text{CO}_2$	0.	0.

Method	Lime required
Rapid Boiler	504.
Lunge-Bilger	560.
Modified Lunge-Bilger	560.

Solution C. To 10 liters of distilled water was added the equivalent of 388 parts per million of lime water which was brought in to solution as  $\text{CaCO}_3$  by means of a current of  $\text{CO}_2$ . On analysis this water showed:

	Amount found	Amount added
Mg	0.	0.
Mineral Acid Hardness	0.	0.
Alkalinity	388.	388.
Free $\text{CO}_2$	12.	12.

Method	Lime required
Rapid Boiler	400.
Lunge-Bilger	450.

The above results show that the lime required as determined from the formula  $\text{Mg} + \text{Alk.} + \text{CO}_2$  is considerably less than the amount shown by the use of excess of lime. Apparently



this difference is independent of the kind of calcium and magnesium salt present.

In order to ascertain whether the lime required, as determined by the rapid boiler method or by the use of an excess of lime was the correct amount to add to a water to properly soften it, a series of fine bottles, each containing one liter of an artificially hard water, was treated with  $\text{Na}_2\text{CO}_3$  equivalent to the mineral acid hardness and varying amounts of lime.

This water at time of treatment showed the following constituents:

Mg as $\text{CaCO}_3$	188.
Mineral Acid Hardness as $\text{CaCO}_3$	330.
Alkalinity as $\text{CaCO}_3$	184.
Free $\text{CO}_2$ as $\text{CaCO}_3$	20.

Lime required by the different methods,

Method	Lime required as $\text{CaCO}_3$
Rapid Boiler	392.
Lunge-Bilger	492.
Modified Lunge-Bilger	492.

After standing 14 hours, the water in this series, treated as described above, was filtered and alkalinity to phenolphthalein and methyl orange was determined in the filtrate. The results obtained are recorded in the following table:



No.	c.c. Lime Water	Mg. lime as $\text{CaCO}_3$	Alkalinity to Phenolphthalein		Alkalinity to Methyl Orange	
			c.c. $\text{H}_2\text{SO}_4$	Pts. per Mil.	c.c. $\text{H}_2\text{SO}_4$	Pts. per Mil.
I.	160	384	1.7	38	3.0	70
II.	175	420	1.6	36	2.4	56
III.	190	456	1.8	42	2.6	62
IV.	205	492	2.1	50	3.0	72
V.	220	528	3.0	73	3.8	93

This experiment shows that the best treatment is obtained when the lime required is calculated from the formula  $\text{Mg} + \text{Alk.} + \text{CO}_2$ .

That there is a discrepancy in the amounts of lime and soda ash required to give the best treatment as determined in the laboratory and in actual practice is well known. In the laboratory calculations are made for reagents of standard strength. In actual practice, however, their strength may vary from time to time as they come from the dealers, besides lime, whether in the form of oxide or hydrate, readily takes up  $\text{CO}_2$  from the air and forms  $\text{CaCO}_3$  which is valueless as a softening agent.

For the purpose of comparing the reagents required and cost of treatment as determined in the laboratory with the amount used and cost in actual practice, samples of raw and treated water from two treating plants on the Illinois Central Railroad was secured. One set of samples was taken from their plant at Mendota, Illinois and the other from Lena, Illinois.

A complete mineral analysis was made on these waters.





They show the following composition:

RAW MENDOTA

IONS		HYPOTHETICAL COMBINATIONS	
Na	30.3	NaNO <sub>3</sub>	4.8
Mg	17.7	NaCl	8.3
Ca	53.4	Na <sub>2</sub> SO <sub>4</sub>	1.9
Fe <sub>2</sub> O <sub>3</sub> +		Na <sub>2</sub> CO <sub>3</sub>	57.7
Al <sub>2</sub> O <sub>3</sub>	1.2	MgCO <sub>3</sub>	61.3
NO <sub>3</sub>	3.5	CaCO <sub>3</sub>	133.2
Cl	5.0	Fe <sub>2</sub> O <sub>3</sub> +	
SO <sub>4</sub>	1.3	Al <sub>2</sub> O <sub>3</sub>	1.2
SiO <sub>2</sub>	10.5	SiO <sub>2</sub>	10.5
Bases	1.0	Bases	<u>1.0</u>
			280.9

TREATED MENDOTA

Na	29.0	NaNO <sub>3</sub>	5.5
Mg	10.0	NaCl	8.3
Ca	12.2	Na <sub>2</sub> SO <sub>4</sub>	3.8
Fe <sub>2</sub> O <sub>3</sub> +		Na <sub>2</sub> CO <sub>3</sub>	52.9
Al <sub>2</sub> O <sub>3</sub>	.5	MgCO <sub>3</sub>	34.6
NO <sub>3</sub>	4.0	CaCO <sub>3</sub>	30.5
Cl	5.0	Fe <sub>2</sub> O <sub>3</sub> +	
SO <sub>4</sub>	2.6	Al <sub>2</sub> O <sub>3</sub>	.5
SiO <sub>2</sub>	8.6	SiO <sub>2</sub>	8.2
Bases	.6	Bases	<u>.6</u>
			144.9



RAW LENA

IONS		HYPOTHETICAL COMBINATIONS	
Na	9.2	NaCO <sub>3</sub>	6.0
Mg	48.9	NaCl	19.3
Ca	107.6	MgCl <sub>2</sub>	4.4
Fe <sub>2</sub> O <sub>3</sub> <sup>+</sup>		MgSO <sub>4</sub>	46.4
Al <sub>2</sub> O <sub>3</sub>	1.0	MgCO <sub>3</sub>	133.0
NO <sub>3</sub>	4.4	CaCO <sub>3</sub>	268.5
Cl	15.0	Fe <sub>2</sub> O <sub>3</sub> <sup>+</sup>	
SO <sub>4</sub>	37.0	Al <sub>2</sub> O <sub>3</sub>	1.0
SiO <sub>2</sub>	13.3	SiO <sub>2</sub>	13.3
Bases	1.3	Bases	<u>1.3</u>
			493.2

TREATED LENA

Na	33.1	NaNO <sub>3</sub>	6.6
Mg	19.8	NaCl	26.4
Ca	3.0	Na <sub>2</sub> SO <sub>4</sub>	62.2
Fe <sub>2</sub> O <sub>3</sub> <sup>+</sup>		Na <sub>2</sub> CO <sub>3</sub>	1.6
Al <sub>2</sub> O <sub>3</sub>	.3	MgCO <sub>3</sub>	68.6
NO <sub>3</sub>	4.8	CaCO <sub>3</sub>	7.5
Cl	16.0	Fe <sub>2</sub> O <sub>3</sub> <sup>+</sup>	
SO <sub>4</sub>	42.0	Al <sub>2</sub> O <sub>3</sub>	.3
SiO <sub>2</sub>	1.7	SiO <sub>2</sub>	1.7
Bases	.9	Bases	<u>.9</u>
			175.8





For the Mendota water

Lbs. per 1000 gal. of  
90% lime

$$\text{Lime required} = .00517(\text{Mg} + \text{Alk})$$
$$'' = .00517(74 + 252) = 1.8$$

No  $\text{Na}_2\text{CO}_3$  is required

Cost of treatment of 1000 gal. at \$.003 per lb.

of lime =  $1.8 \times .003$  = \$0.0054

For the Lena water

Lbs. per 1000 gal. of  
90% lime

$$\text{Time required} = .00517(203 + 388) =$$

3.0  
Lbs. per 1000 gal. of  
95%  $\text{Na}_2\text{CO}_3$

Soda ash required = .0092(M. A. H.)

. " " " = .0092 ( 43) 0.4

Cost of lime treatment per 1000 gal. = \$.009

Cost of soda treatment per 1000 gal.

$$\begin{array}{rcl} \text{at } \$.01 \text{ per lb.} & = & \underline{\hspace{1cm} .004 \hspace{1cm}} \\ & & \$.013 \end{array}$$

Mr. C. E. Thomas, General Foreman Waterworks, Illinois Central Railroad, reports\* that at Mendota they use 2.8 lbs. of

\*In a communication to Dr. E. Bartow, Director State Water Survey.

lime per 1000 gallons at a cost of \$.0106 per 1000 gallons for treatment. At Lena they use 3.12 pounds of lime per 1000 gallons and .56 pounds of soda ash per 1000 gallons at a cost of \$.0157 per 1000 gallons for treatment.

In the case of either water the amount of reagents used and cost of treatment are greater in actual practice than that



determined in the laboratory. This may be partly accounted for by the fact that the reagents used contain an excessive amount of impurities and also to the lack of proper control. We hope further investigations along this line may be made.

In making an analysis by the rapid method the negative ions determined are chlorine and the carbonate radicle, and in making hypothetical combinations from the data thus obtained chlorine is calculated to sodium chloride and the mineral acid hardness to sulphates of calcium and magnesium. That this is sometimes misleading is apparent from the following analysis:

Laboratory No. 20582

Constituents determined		Combinations	
Solids	398.	NaNO <sub>3</sub>	83.
Alkalinity	94.	NaCl	16.
Chlorine	30.	MgCl <sub>2</sub>	27.
Sulphate	140.	MgSO <sub>4</sub>	91.
Nitrate	6.	CaSO <sub>4</sub>	95.
Total Magnesium	104.	CaCO <sub>3</sub>	<u>94.</u>
M. A. H.	174.		406.

If the mineral acid hardness had consisted of sulphates of calcium and magnesium the above would have been a fair water for boiler use, but as sulphates are not present in sufficient amounts to equal the mineral acid hardness, MgCl<sub>2</sub> is present. This is very corrosive when used in boilers.

It is obvious from above example that a knowledge of total SO<sub>4</sub> is essential in order to form an intelligent opinion as to the quality of a water. Some work was, therefore, done on the volumetric determination of sulphates in water.



The first method tried was suggested by Dr. Holmes of the University of Illinois. In this method  $\text{BaC}_2\text{O}_4$  is added to a sample of the water.  $\text{BaSO}_4$  is found together with a corresponding amount of soluble oxalate which is determined by oxidation with standard  $\text{KMnO}_4$  solution. This method was first tried on standard  $\text{H}_2\text{SO}_4$  solution. The following procedure was carried out.

51 c.c. N/50  $\text{H}_2\text{SO}_4$  was run into a 200 c.c. graduated flask, the volume made up to about 100 c.c. About one gram  $\text{Ba}_2\text{C}_2\text{O}_4$  was added and the solution boiled for some time. The solution was then made up to 200 c.c. and cooled. It was then filtered and 50 c.c. withdrawn, sulphuric acid added, heated to boiling and titrated with  $\text{KMnO}_4$  of such a strength that 1 c.c. equaled 0.00365  $\text{SO}_4$ . Blank tests were run with the sample and its reading subtracted from the reading of the sample. With standard  $\text{H}_2\text{SO}_4$  the following results were obtained:

	$\text{SO}_4$ present	$\text{SO}_4$ found
NO. I. 51 c.c. N/50 $\text{H}_2\text{SO}_4$	.049	.051
NO. II. 51 c.c. N/50 $\text{H}_2\text{SO}_4$	.049	.051

When only  $\text{H}_2\text{SO}_4$  was used good results were obtained, but when a water of known sulphate contents was tried very unsatisfactory results were obtained.

For the purpose of studying the interference four solutions were made up.

Solution I contains 1.8 grams NaCl in 1000 c.c. distilled water		
Solution II contains 1.0 grams $\text{MgCl}_2$ in 1000 c.c.	"	"
Solution III contains 10. grams $\text{MgSO}_4$ in 1000 c.c.	"	"
Solution IV contains 0.41 grams $\text{CaCO}_3$ in 1000 c.c.	"	"





The following table shows the results of this study of interference:

No.	c.c. N/50 H <sub>2</sub> SO <sub>4</sub>	c.c. Sol.I	c.c. Sol.II	c.c. Sol.III	c.c. Sol.IV.	SO <sub>4</sub> present	SO <sub>4</sub> found
1	51	100	----	----	----	49.	47.
2	51	100	50	----	----	49.	47.
3	--	---	--	25		50.	52.
4	51	---	50	----	----	49.	47.
5	51	50	50		100	49.	28.
6	51	100	----	----	100	49.	37.

The above show that there was little interference where NaCl, MgCl<sub>2</sub> or MgSO<sub>4</sub> was present, but the end-point was difficult to obtain as it had a tendency to lag. The presence of CaCO<sub>3</sub> makes this method unreliable. As there are no means of completely removing calcium the method was abandoned without any more work.

A method\* originally used for determinations of sulphur in pyrites and describes by F. Raschig<sup>o</sup> depending on the formation

---

\*Z. angen. Chem. 19, 331.

---

<sup>o</sup>The Chemical Engineer. Vol. IV. June, 1906, p. 76.

---

of insoluble benzidine sulphate which is filtered off and titrated with a standard alkalie.

The solutions required are:

Benzidine solution.

One per cent hydroxyl amine hydrochloride solution

Standard alkalie solution.

The benzidine solution is made as follows:



8 grams benzdine is rubbed up with 8 c.c. water, the pulp is brought with 150 c.c. of water into a liter flask. 10 c.c. concentrated HCl is added and the whole made up to 200 c.c. In a short time everything dissolves to a brown liquid, which is filtered if necessary. This is then made up to 4 liters. 150 c.c. of this dilute solution is sufficient to precipitate .1 grams  $H_2SO_4$ .

The procedure is as follows:

That amount of water was taken which gave about 20 mgs. of  $SO_4$ . To this was added 10 c.c. of the 1%  $NH_2OH$  HCl solution and 100 c.c. benzdine solution. After standing 15 minutes the precipitate was filtered off rapidly by means of a suction filter, washed once with the mother liquor and finally with 10 c.c. of water. The precipitate was never allowed to become completely dry. Precipitate and filter paper was then washed into the beaker in which the precipitation took place, heated to boiling and titrated with N/20 NaOH using phenolphthalein as indicator. The following results were obtained by this method:

Number	Gravimetric $SO_4$ present in milligrams	Volumetric $SO_4$ found in milligrams
N/50 $H_2SO_4$	24.4	24.0
18761	158.0	145.0
19041	1918.	1907.
19906	199.	190.
19928	125.	115.
20399	99.	93.
20400	218.	207.

The results show that this method is accurate enough for our purpose and the fact that the time required to make one





determination need not be over 30 minutes makes this a very satisfactory method.

It is sometimes desirable to know approximately the amount of alkalies present in a water. This may be accomplished as follows:

The residue from the determination of total solids is moistened with concentrated  $H_2SO_4$ , the excess driven off over a free flame. This operation changes all the bases to sulphates which are dissolved in 200 c.c. distilled water and the sulphates determined as above described.

The following are examples of alkalies determined gravimetrically and indirectly from total bases:

Laboratory No. 20445.

Constituents determined		Combinations	
Total Solids	1125.	$NaCO_3$	10.
M. A. H. as $CaCO_3$	9.0	$MgCO_3$	94.
Mg. as $CaCO_3$	112.0	$CaCO_3$	128.
Wt. of total bases as sulphate		1328.	
$SO_4$ from total bases		876.	
Mg. and Ca. calculated to sulphates		309.	
$SO_4$ remaining to go with alkalies		646.	
$SO_4$ as $Na_2SO_4$		955.	
Calculated to Na we have		310.	
Na from mineral analysis		316.	
Cl		280.	
$SO_4$		274.	
$SO_4$ in total bases		876.	
Solids		1125.	



Calculations.

Mg to $\text{MgSO}_4$	126.	
$\text{SO}_4$ required for Mg		100.
Ca to $\text{CaSO}_4$	173.	
$\text{SO}_4$ required for Ca		<u>122.</u>
$\text{SO}_4$ used		222.
$\text{SO}_4$ found in total bases		876.
		<u>222.</u>
$\text{SO}_4$ to go to $\text{Na}_2\text{SO}_4$		654.
As $\text{Na}_2\text{SO}_4$	968.	
Total Na	<u>654.</u>	
	314.	

IONS		HYPOTHETICAL COMBINATIONS	
Na	314.	$\text{NaCl}$	462.
Mg	26.	$\text{Na}_2\text{SO}_4$	405.
Ca	51.	$\text{Na}_2\text{CO}_3$	7.
Cl	280.	$\text{MgCO}_3$	90.
$\text{SO}_4$	274.	$\text{CaCO}_3$	<u>128.</u>
			1092.
		Total Solids	1125.

This leaves 33 parts not accounted for. Part of this is due to solica, but it must also be remembered that residue on evaporation is always higher than the sum of the mineral constituents, due probably to water not driven off and organic matter.

By the foregoing operations we have a rapid, fairly accurate volumetric method for the determination of all the common



constituents in a water. The whole procedure may be carried through in about one hours time. The material thus obtained can be used to calculate the hardness, the treatment, etc., and hypothetical combinations can also be made. Much of this data, however, would be of little value unless we can combine them into salts probably found in the water.

A rational method of hypothetical combination--because it shows us the character of the water, its action on boilers, etc--is the one used in the laboratory of the Illinois State Water Survey.

The ions are combined in the following order:

Na	NO <sub>3</sub>
Mg	Cl
Ca	SO <sub>4</sub>
	CO <sub>3</sub>

The for purpose of testing a water after treatment to determine whether it has been properly treated or not it is sufficient to determine alkalinity to phenolphthalein and methyl orange. If the phenolphthalein alkalinity is more than one-half total alkalinity, hydrates are present and the water has been over-treated. If phenolphthalein alkalinity is less than one-half total alkalinity the water has been undertreated. The best treatment will show phenolphthalein alkalinity equal to one-half the total alkalinity.

A properly treated water should show no coloration on the addition of phenolphthalein to a sample of the water to which has been added a few crystals of BaCl<sub>2</sub>. If a color appears the amount of hydrate present may be determined by titrating with a standard HCl solution.





A water having permanent hardness should after treatment, show M. A. H. equivalent to zero.



## SUMMARY.

The various purposes for which water is used have been reviewed and the disadvantages of a hard water for different industrial purposes have been shown.

Waters have been classified according to their most important constituents and examples of each class given.

Different methods of analysis have been tested and methods of calculating reagents have been tried.

Stabler's formula for calculating from ions can be simplified.

Kimberly's method of analysis is unnecessarily long and the method of calculation complicated. In a magnesia water the M. A. H. does not necessarily contain  $\text{CaSO}_4$  which is the contention of Kimberly.

J. O. Handy's method of calculating lime is founded on a wrong principle.

The potassium stearate method is impractical.

The method of analysis proposed by Wartha and Pfeifer is rapid and as to accuracy compares favorably with the gravimetric method. From the data thus obtained calculations of reagents required can be made by means of a very simple formula. The amount of lime required to treat a water cannot be learned by adding an excess of lime and determining the excess. The results obtained are always too high.

A comparison between reagents required and cost of treatment as determined in the laboratory and in actual practice shows that lower results are obtained in the laboratory.

A satisfactory and rapid method has been found for the





determination of sulphates in water.

The alkalies can be determined quite accurately by an indirect method.

In general, a rapid, complete and sufficiently accurate method has been devised for determining the constituents required in an analysis to control of water softening.



BIBLIOGRAPHY.

American Institute of Mining Engineers  
Chemiker Zeitung  
Christie, W. W. Boiler Waters.  
Clark, F. W. Data of Geochemistry  
Collet, H. Water Softening  
Dole, R. B. Water Supply Paper No. 236  
Engineering  
Engineering News  
Journal of Infectious Diseases, Supplement  
Metallurgical and Chemical Engineer  
Purification of Water for Boiler Feeding.  
Harrison Safety Boiler Works Company  
Railroad Gazette  
Stillman, Thos. B. Engineering Chemistry  
U. S. G. S. Bulletin, No. 330.  
Whipple, G. C. The Value of Pure Water  
Zeitschrift fur Angewandte Chemie  
Booth, W. H. Water Softening.









UNIVERSITY OF ILLINOIS-URBANA



3 0112 079825953